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INVENTORS:

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ISSUED:

July 6 , 1965

FILED:

LAID OPEN:

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23/190

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CLAIMS: [Show all claims](#)

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1 This invention relates to a process for the
2 manufacture of hydrated calcium silicates. More
3 particularly, the invention relates to a process for
4 the manufacture of dicalcium silicate alpha hydrate.
5 Still more particularly, the invention relates to a
6 process for the manufacture of dicalcium silicate alpha
7 hydrate wherein substantially no additional materials
8 or contaminants are formed. The product obtained has
9 found very effective use as a flattening agent for clear
10 lacquers.

11 HISTORY

12 Because of its importance in the curing of
13 portland cements and other fields, the calcium oxide-
14 silicon dioxide-water system has received considerable
15 attention in the technical fields during the past
16 several decades. Several different methods have been
17 devised whereby synthetic calcium silicates are com-
18 mercially produced. The two most prominent methods
19 of synthesis are the precipitation method and the
20 hydrothermal method. The former method generally
21 results in the production of an amorphous type calcium
22 silicate and is accomplished by reacting a calcium salt
23 such as calcium chloride with a water solution of an
24 alkali silicate such as sodium silicate. A precipitated
25 calcium silicate results.

26 On the other hand, several crystallographically
27 different hydrated calcium silicate phases have been
28 prepared by hydrothermal methods of synthesis. This
29 reaction is effected under high temperature by causing
30 a CaO source, such as lime, to react with a SiO₂ source,
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1 such as diatomaceous earth, in the presence of water.
2 Compounds covering calcium oxide to silicon dioxide
3 ratios of 0.5 to 3.0 have been produced by the many
4 workers in this field. When lime and silica (amorphous
5 or crystalline) are reacted at a CaO/SiO_2 mol ratio
6 of 2 with an excess of water in the temperature range
7 of 180°C . to 300°C ., only one thermodynamically stable
8 phase is formed. This phase is identical in all proper-
9 ties to the mineral hillebrandite and has the composi-
10 tion $2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$. It is also properly considered to
11 have the formula $\text{Ca}_2(\text{SiO}_3\text{OH})\text{OH}$.

12 Another thermodynamically unstable phase
13 having essentially the same chemical composition as
14 hillebrandite was discovered as a by-product in port-
15 land cement which had been steam cured in the tempera-
16 ture range of 150 to 175°C . This phase is entirely
17 different from the mineral hillebrandite in its optical
18 properties and has a X-ray diffraction pattern different
19 from any other hydrated calcium silicate. This phase
20 has been given the name dicalcium silicate alpha hydrate.
21 The resulting structure can be described as orthorhombic
22 prisms which are colorless and transparent with a luster.

23 Since the time of its discovery, various
24 workers have demonstrated that the alpha hydrate can
25 be prepared in good yields by hydrolysis of beta calcium
26 silicate, $2\text{CaO}\cdot\text{SiO}_2$, over a temperature range of 140
27 to 200°C . They have also shown that the hydrolysis of
28 tricalcium silicate, $3\text{CaO}\cdot\text{SiO}_2$, over the temperature
29 range of 120 to 200°C . gives mixtures of calcium hydroxide
30 and dicalcium silicate alpha hydrate.
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1 However, to my knowledge no one has to this
2 date succeeded in preparing the alpha hydrate in good
3 yield by the direct hydrothermal reaction of silicon
4 dioxide, in any of its physical forms, with calcium
5 hydroxide. One attempt has been recorded using a lime
6 to silica ratio of 2:1 at a temperature of 200°C., but
7 the time consumed amounted to 28 days and with the
8 result that only a trace of dicalcium silicate alpha
9 hydrate was formed in addition to several other products.

10 OBJECTS

11 It is therefore the primary object of this
12 invention to provide a method of hydrothermally producing
13 dicalcium silicate alpha hydrate whereby good yields are
14 obtained.

15 It is a further object of this invention to
16 provide a method of efficiently producing dicalcium
17 silicate alpha hydrate in a substantially uncontaminated
18 condition.

19 It is still another object of this invention
20 to provide a method of producing dicalcium silicate
21 alpha hydrate under controlled reaction conditions where-
22 by the production of other hydrated calcium silicates
23 is reduced to a minimum.

24 It is another object of this invention to
25 provide a dicalcium silicate alpha hydrate which possesses
26 properties useful in commercial applications.

27 Other objects and further scope of applicability
28 of the present invention will become apparent from the
29 detailed description given hereinafter; it should be
30 understood, however, that the detailed description,
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1 while indicating preferred embodiments of the invention,
2 is given by way of illustration only, since various
3 changes and modifications within the spirit and scope
4 of the invention will become apparent to those skilled
5 in the art from this detailed description.

6 BRIEF DESCRIPTION OF INVENTION

7 It has been discovered that the production
8 of substantially pure alpha hydrate calcium silicate
9 is effected when the hydrothermal reaction of calcium
10 hydroxide and silica is carried out in the presence of
11 a small amount of sodium hydroxide or sodium fluoride.

12 The use of sodium hydroxide or sodium fluoride
13 to promote the formation of the metastable phase of the
14 dicalcium alpha hydrate is believed to be unique in the
15 art. Heretofore reagents of this type have been con-
16 sidered to be simple catalysts which had no influence
17 on the product which would be formed.

18 It has been further determined that the
19 various reaction conditions, e.g., temperature, mol,
20 ratio, etc., may be controlled within preferred ranges
21 to give the most favorable formation of the end-product.

22 DETAILED DESCRIPTION OF INVENTION

23 Work was carried out in the laboratory to
24 determine the proper reaction conditions to produce
25 substantial yields of dicalcium silicate alpha hydrate.
26 The CaO/SiO_2 mol ratio was varied over the range of
27 about 1.5 to about 2.2 and temperatures employed above
28 about 180°C. In so reacting these two basic constituents,
29 the alpha hydrate form always appeared among the final
30 reaction products but only in minor amounts. Further,
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1 even at a mol ratio of exactly 2:1, the compound,
2 although always present, was always contaminated with
3 other hydrated calcium silicates.

4 Work was then conducted in accordance with
5 the instant invention, wherein small amounts of sodium
6 hydroxide or sodium fluoride were added to the hydro-
7 thermal mixture of silica and calcium oxide containing
8 materials. This new reaction produced surprising results
9 in that the final product was a substantially uncon-
10 taminated alpha hydrated calcium silicate.

11 With regard to the reaction conditions used,
12 temperatures above 180°C. with corresponding reaction
13 times up to about 4 hours are preferred. Higher tempera-
14 tures result in a faster reaction rate with the upper
15 limits being set by the pressure which the reactor can
16 withstand. The CaO/SiO_2 mol ratio is preferably within
17 the range of 1.8:2.2 to produce the least contaminated
18 product.

19 Various sources of the reactants can be used.
20 With regard to the silicon dioxide, any siliceous-like
21 material, which contains substantial amounts of silica
22 that is capable of reacting with an alkaline earth hydroxide
23 is applicable. Examples of such materials are silica sand,
24 silica gel, diatomaceous earth, or the like. The amorphous
25 type of the silica is preferred, however, because of its
26 higher reactivity. The usual source of the calcium
27 hydroxide in its reaction with silica may be used. Such
28 materials include quick lime, wet or dry slaked lime,
29 etc.
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1 The sodium hydroxide or sodium fluoride may
2 be added in amounts of between about 0.10 to 10.0% or
3 more by weight of the reactants with due consideration
4 being given when higher amounts are employed to side
5 reactions and the possibility of contaminants. I have
6 found about 2.0% to about 3.0% by weight of the reactants
7 to be effective as well as practical.

8 As the initial step in the process, finely
9 divided lime and silica are suspended in at least enough
10 water to form a pumpable slurry. The lime and silica
11 may be suspended individually or they may be blended
12 before pumping into the reaction vessel. The sodium
13 hydroxide or sodium fluoride may be added with either
14 of the components or it may be added individually.
15 Likewise mixtures of the two may be used.

16 The following examples illustrate the invention:

17 EXAMPLE I

18 A slurry of silica was prepared by mixing
19 finely ground diatomaceous earth with water so that the
20 slurry contained 0.87 lb. solids per gallon. A slurry
21 of hydrated lime was prepared by mixing hydrated lime
22 with water so that the slurry contained the equivalent
23 of 1.41 lbs. of CaO per gallon. The lime slurry also
24 contained 48 lbs. of NaOH per 1000 lbs. of CaO. One
25 thousand two hundred and fifty-eight gallons of the
26 diatomaceous earth slurry were pumped into the reactor
27 where it was heated by direct injection of steam. Water
28 was used to flush the feed lines. Then 1488 gallons of
29 the lime slurry were pumped into the reactor, likewise
30 followed by water to flush the lines. The reaction
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1 vessel was continually agitated and held at the desired
2 temperature of 232°C. by injection of steam. The
3 slurry was reacted for one hour and ten minutes at 232°C.
4 and then discharged through a cooling system into an
5 appropriate collecting tank. The solids were filtered
6 from the slurry and then air dried and ground. The
7 finished product was identified as dicalcium silicate
8 alpha hydrate by X-ray diffraction and had the following
9 physical properties.

10	Bulk density	13.7 lb./ft.
11	Gardner-Coleman	
	water adsorption	135%
12	pH of 10% slurry	10.8
	Wet density	20.3 lb./ft.

13 The example was rerun using sodium fluoride with sub-
14 stantially the same results.

15 It should be appreciated that the procedure
16 outlined in Example I in no way limits the invention to
17 these particular conditions. Alternative methods of
18 heating and order of addition of the reactants to the
19 reactor could have been used. Basically, the process
20 requires that the proper amounts of hydrated lime and
21 reactive silica be reacted in a water medium at the
22 desired temperature for the required period of time.

23 The dicalcium silicate alpha hydrate which is
24 produced by the process described in Example I shows
25 good performance as a flattening agent for furniture
26 lacquers. This application is illustrated by Example II.

27 EXAMPLE II

28 One hundred grams of the dicalcium silicate
29 alpha hydrate, as prepared in Example I, were mixed with
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1 a sufficient quantity of a clear nitrocellulose lacquer
2 base to give 100 g. of vehicular solids. Sufficient
3 lacquer thinner was added to thin the mixture to a
4 viscosity of about 1000 centipoises. This mixture was
5 ground in a ball mill until the dicalcium silicate alpha
6 hydrate had reached a Hegman fineness of 6-1/2. After
7 grinding, sufficient clear lacquer base was added to
8 reduce the amount of dicalcium silicate alpha hydrate
9 to 10% by weight of the lacquer vehicular solids.
10 Sufficient thinner was then added to reduce the flattened
11 lacquer to spraying viscosity (50 centipoises). The
12 formulation was then sprayed on a test panel and dried
13 in the usual manner.

14 After drying, the lacquer film was found to
15 have satisfactory transparency and gave a Gardner 60°
16 specular gloss reading of 15. The lacquer was tested
17 without the dicalcium silicate alpha hydrate and gave
18 a Gardner reading of between 50 and 60 with a perfect
19 mirror reading being 100.
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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of hydrothermally producing dicalcium silicate alpha hydrate comprising hydrothermally reacting silicon dioxide and a calcium oxide producing material in the presence of a compound selected from the group consisting of sodium hydroxide and sodium fluoride.

2. A method of hydrothermally producing dicalcium silicate alpha hydrate comprising hydrothermally reacting silicon dioxide and calcium oxide producing material in the presence of a compound selected from the group consisting of sodium hydroxide and sodium fluoride wherein a CaO/SiO_2 mol ratio from about 1.5 to about 2.2 is used.

3. A method of hydrothermally producing dicalcium silicate alpha hydrate comprising hydrothermally reacting silicon dioxide and calcium hydroxide in the presence of a compound selected from the group consisting of sodium hydroxide and sodium fluoride wherein a reaction temperature of above about 180°C . is used.

4. A method as described in claim 3 wherein about 2 to about 3% by weight of the reactants of the added compound is employed.

5. A method of hydrothermally producing dicalcium silicate alpha hydrate comprising hydrothermally reacting calcium hydroxide and silicon dioxide in a CaO/SiO_2 mol ratio of 2:1 in the presence of about 2 to about 3% by weight of the reactants of a compound selected from the group consisting of sodium hydroxide and sodium fluoride.

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6. A method of hydrothermally producing dicalcium silicate alpha hydrate comprising hydrothermally reacting silicon dioxide and calcium hydroxide in the presence of sodium hydroxide.

7. A method of hydrothermally producing dicalcium silicate alpha hydrate comprising hydrothermally reacting silicon dioxide and calcium hydroxide in the presence of sodium fluoride.

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